보건학석사 학위논문

Analysis of the Photoresist and Its Possible By-product Used in Semiconductor Manufacturing Industries

반도체 제조 공정에서 사용하는 포토레지스트의 성분 및 발생 가능한 부산물 분석

2016년 8월

서울대학교 보건대학원

환경보건학과 산업보건전공

장 미 연

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이 논문을 보건학석사 학위논문으로 제출함

2016 년 5 월

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장미연의 보건학석사 학위논문을 인준함

2016 년 7 월

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ABSTRACT

Analysis of the Photoresist and Its Possible By-product Used in Semiconductor Manufacturing Industries

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Objective The semiconductor industry is known to use various chemicals but little is known. Especially, numerous chemical compounds including organic solvents and trade secrets have been used in photolithography process. The purpose of this study was to identify the chemical constituents of photoresist products and their by-products, and to compare the constituents with material safety data sheets (MSDS) and analytical results.

Methods A total of 51 photoresists with 48 MSDS were collected from 4 companies. Analysis consisted of two parts; first, the constituents of the chemical products were identified with MSDS and organic solvents were analyzed by the gas chromatography with mass spectrometer (GC/MS) for qualitative evaluation and gas chromatography with flame ionization detector (GC/FID) for quantitative analysis. Second; for verification of by-product of the chemical products, analysis was performed by headspace solid-phase microextraction (HP-SPME) with GC/MS. The 75 ㎛ carboxen /polydimethylsiloxane (CAR/PDMS) fiber for VOCs and the 65 ㎛ polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber for formaldehyde were used. The chemical constituents were categorized according to its hazard indices carcinogen, mutagen, reproductive toxicant, and trade secret.

Results Forty-five out of 48 (94%) products contained trade secrets, and its amount range was from 1 to 65%. A total of 238 ingredients with multiple counting (35 ingredients removing multiple counting) were identified in MSDS of 48 products and 48.7% of ingredients were labeled as a trade secret. In the result of analysis, 5 ingredients which should not be designated as a trade secret by Korea Occupational Safety Health Act (KOSHAct) were detected and not specified their toxicological information in MSDS, and the concordance rates between MSDS and analytical result was 41.7%. In the result of the analysis of by-products, 129 chemicals classified according to CAS No. were detected, and 17 chemicals were CMRs. Also formaldehyde was released from 12 of 21 products which use novolak resin.

Conclusion We confirmed that several photoresists contain carcinogens, and some were not specified their toxicological information in MSDS. Also, hazardous chemicals including benzene and formaldehyde were released from photoresist products as the by-products. Therefore, it is necessary to establish a systematic management system of chemical compounds and the working environment.

Keywords: Semiconductor, Photolithography, Photoresist, By-product, Trade secret, MSDS, SPME-GC/MS.

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1. Introduction

Semiconductor, as an intermediate substance which has both properties of a conductor and nonconductor, has typically electric resistance, but as injection of specific impurity or application of heat, it has electric conductivity.

The three main processes of the semiconductor industry consist of wafer manufacturing, fabrication, and packaging. Wafer manufacturing uses silicon (Si) extracted from silicon dioxide (SiO_2). Fabrication (Fab) adjusts the circuit pattern on wafer through specific processes. The packaging process assembles chips from cutting wafers. Fab processes - which use numerous chemicals - is divided into several sequences: oxidation, photolithography, etching, and stripping (Wald et al., 1987, Chelton et al., 1991, Quirk et al., 2001, Marano et al.,2010, Park et al., 2011).

Photolithography, which has the highest chemical usage in Fab, involves 3 major steps: photoresist coating, exposure, and develop. As a large amount of chemicals are used in photolithography, this increases exposure to hazardous factors. Organic solvents and acid are used for cleaning, photoresist coating, and developing. Also the by-products can released by ultraviolet (UV) light and heat during the developing process. Among these hazardous factors, photoresist (PR) consists of polymer, solvent, sensitizer, and additives. It is classified as a positive and negative photoresist in accordance with response to light, and most of chemical constituents are specified as a trade secret; it is as the private property of company also called undisclosed information or know-how (Wald et al., 1987, Chelton et al., 1991, Hallock et al., 1995, Park et al, 2011).

Due to the lack of information arisen from secrecy, little is known with regard to record of exposure to hazardous factor in semiconductor industry. In particular, it is hard to distinguish hazardous factor from surround environment because Fab process is performed in the cleanroom. Also, it is difficult to know chemical information due to lack of sufficient information, secrecy in know-how and fast-changing technology. However, it is necessary to evaluate the past exposure information, such as transition of chemicals, process technology and management technique, for investigation about the exposure of hazardous factor (Park et al, 2011, Yoon, 2012).

Although the studies related to occupational disease in the semiconductor industry have been conducted, the logical bases which can acknowledge the correlation between task and disease have been insufficient. It is hard to realize the hazardous factors that employees may be exposed to, if it does not proceed to identify the constituents of chemical compounds (Marano et al., 2010). Thus, it is necessary to investigate the chemical constituent and toxicological information through material safety data sheets (MSDS). Research shows more than 40% of chemical products used in the manufacturing industry contained trade secrets in Korea (OSHRI, 2009). Subsequently, comparisons between the MSDS and product analyses that detail the chemical composition of products need to occur (Welsh et al., 2000).

Carcinogenic risk in the semiconductor industry is widely known, whereas studies identifying chemicals used in the semiconductor industry processes have not been conducted. Consequently, it is necessary to investigate the chemical constituents of chemical products for the protection of the employee’s health, establish a systematic management system of chemicals products, and further study the correlation between chemical exposure and disease.

The aim of this study is to identify the chemical constituents of photoresist products and their by-products, and compare with the MSDS and analytical results.

2. Materials and Methods

2.1. The outline of this study

The methodological outline of this study is shown in Figure1. A total of 51 photoresist products were used in this study. The first step was to review MSDS in order to confirm basic information such as supplier, resin type, chemical constituent and existence of trade secret materials. The second section was to analyze organic solvents contained in photoresists and their possible by-products. The chemical analysis consisted of both a qualitative and quantitative method. The qualitative analysis was performed to identify the chemical constituents in the products and then quantitative analysis was performed to identify the Carcinogen, Mutagen, Reproductive toxicant substances (CMRs) and toxic materials, also qualitative analysis of possible by-products was simultaneously conducted. Finally, the work comparing the results acquired from instrumental analyses and MSDS were conducted.

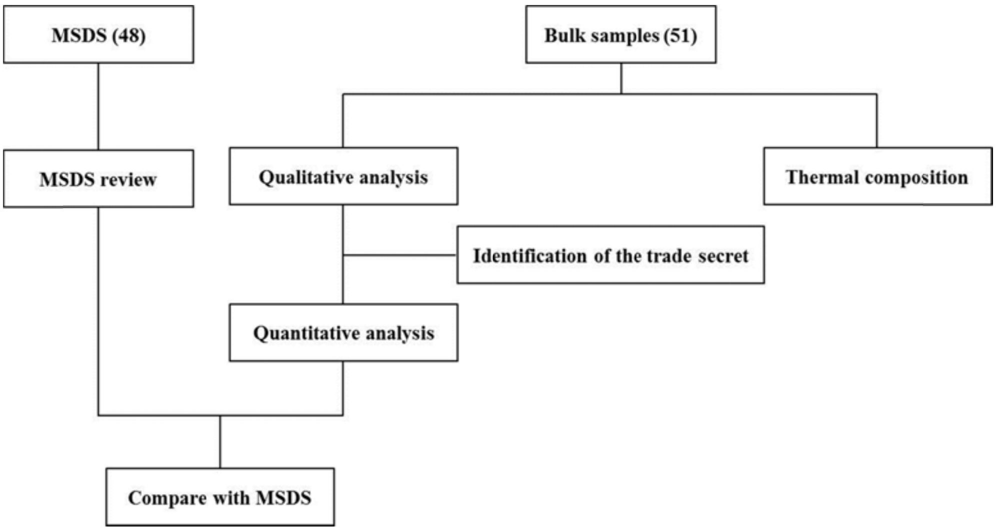

Figure 1. The outline of this study.

2.2. Identification of the photoresist

2.2.1. Analytical method

A total of 51 photoresist products used in the fabrication process were collected with its MSDS in convenience sampling from 3 companies and 1 academic semiconductor research center in Korea. MSDS of three chemical products were not available (Table 1). Photoresist products were provided by 15 suppliers from 3 different countries; 31 products from Korea, 16 from Japan, 4 from United States (US). Over 60% of products were provided after 2010 and the oldest products were provided in 2004. The volatile constituents, which could be analyzed by gas chromatography (GC, 7890A, Agilent Technology, USA)-mass spectrometer (MS, 5975C Series, Agilent Technology, USA)or gas chromatography (GC, 6890N, Agilent Technology, USA) with flame ionization detector (FID), of 51 products were qualitatively identified and some of them were quantitated to compare its results with the lists in MSDS.

Table 1. The numerical information on the photoresist products in this study

Company	Total Product	MSDS Not Provided
A	26	1
B	7	2
C	9	0
D	9	0
Total	51	3

2.2.2. Qualitative analysis

Organic solvents contained in photoresist products were analyzed after dilution with 1/100 of carbon disulfide (CS_2, Kanto, Japan) and methanol (99.8%, Sigma Aldrich, USA), respectively. Diluted samples were sonicated for 30 minutes at room temperature and viscous chemical samples were filtrated through the Nylon Syringe filter (13 mm, 0.2 μm, Whatman, USA). Qualitative analysis was conducted by GC/MS in a scan mode between m/z 35 and 350. A volume of 1 μl extracted sample was injected on the split mode (50:1) by auto sampler (Combi PAL, CTC analytics, Switzerland). DB-5MS column which has 30 m in length, 0.25 mm in inner diameter, 0.25 μm in film thickness was used for analysis (122-5532, Agilent Technology, USA). GC was programmed to maintain the initial temperature at 40 ℃ for 3 minutes, and then 10 ℃/min to 250 ℃ for 2minutes. The injector and MS interface temperature were set at 260 ℃ and 280 ℃, respectively. Helium (99.99%, purity) was used as a carrier gas with a constant flow rate of 1 ml/min. Mass spectrometer were obtained under electron ionization mode (EI) at 70 eV and the quadrupole and ion source temperature were 150 ℃ and 250 ℃, respectively. Each mass spectrum was matched up with GC-MS library (W10N11), and the chemical matching rate selected was higher than 80percent. The specific GC-MS conditions were shown in Appendix 1.

2.2.3. Quantitative analysis

We performed sample pretreatment in identical methodology with qualitative analysis. Quantitative analysis was conducted by GC/FID and auto sampler (7683B Series, Agilent Technology, USA). The chemical for quantitative analysis was selected in the detected chemical from qualitative analysis, which also be listed in MSDS or has toxicity if not listed in MSDS. A volume of 1 μl extracted sample was injected on split mode (50:1). EN-5 column which has 30 m in length, 0.25 mm in inner diameter, 0.25 μm in film thickness was used for analysis (053139, SGE Analytical Science, Australia). GC was programmed to maintain the initial temperature at 40 ℃ for 3 minutes, and then 10 ℃/min to 250 ℃ for 2 minutes. Inlet and detector temperature are 260 ℃and 280 ℃, respectively. Helium (99.99%, purity) was used for carrier gas and flow rate was 1 ml/min. The specific GC-FID conditions were shown in Appendix 2.

2.3. By-products of the photoresists

2.3.1. Volatile organic compounds (VOCs)

We performed analysis for volatile organic compounds (VOCs) released from the photoresist as the by-product, using headspace solid-phase microextraction (HP-SPME, Combi PAL, CTC analytics, Switzerland) with GC/MS in scan mode between m/z 35 and 225. One hundred milligrams of the bulk sample was sealed in a 20 ml amber headspace glass vial with an aluminum-coated polytetra fluoroethylene (PTFE)/silicone septum. The 75 μm carboxen/polydimethyl siloxane (CAR/PDMS) SPME fiber was used. The vial was placed into a heating block set to 110 ℃ for 3 minutes and then SPME fiber was inserted into the vial for adsorption. Afterward, the SPME fiber was transferred into the injector of the GC for thermal desorption at 250 ℃ for 5 minutes. DB-5MS column which has 30 m in length, 0.25 mm in inner diameter, 0.25 μm in film thickness was used (122-5532, Agilent Technology, USA). The temperature of column was programmed from 40 ℃ for 3 minutes hold, at 10 ℃/min to 250 ℃. Helium (99.99%, purity) was used as a carrier gas with a constant flow of 1 ml/min. MS interface was set at 260 ℃, and the quadrupole and ion source temperature was kept at 150 ℃ and 250 ℃, respectively. Each mass spectrum was matched up with GC-MS library (W10N11), and the chemical matching rate selected was higher than 80 percent. The specific GC-MS conditions were shown in Appendix 3

2.3.2. Formaldehyde

The experiment was performed to determine whether the formaldehyde emission from novolak resin by HS/SPME-GC/MS was used in the selected ion monitoring (SIM) mode set for m/z 29 and 30. Fifty hundred milligrams of the bulk sample was sealed in a 20 ml amber headspace glass vial with an aluminum-coated polytetrafluoroethylene (PTFE)/silicone septum. The 65 μm polydimethylsiloxane /divinylbenzene (PDMS/DVB) SPME fiber was used. The vial was placed into a heating block set to 180 ℃ for 3 minutes and then SPME fiber was inserted into the vial for adsorption. Afterward, the SPME fiber was transferred into the injector of the GC for thermal desorption at 200 ℃ for 5 minutes. DB-WAX column which has 30 m in length, 0.25 mm in inner diameter, 0.25 μm in film thickness was used for analysis (122-7032, Agilent Technology, USA). The temperature of column was programmed from 35 ℃ for 5 minutes hold, at 10 ℃/min to 180 ℃. Helium (99.99%, purity) was used as a carrier gas with a constant flow of 1 ml/min. MS interface was set at 210 ℃, and the quadrupole and ion source temperature was kept at 150 ℃ and 250 ℃, respectively. The specific GC-MS conditions were shown in Appendix 4.

2.4. Quality control

Quality control was conducted to evaluate the accuracy and precision of analysis. Reproducibility of analytic instrument was evaluated before and after analysis, and used 7 chemicals. Relative standard deviations (%RSD) were acquired by analyzing the 3 μl of stock solution in 1ml CS_2 10 times repetitively. We confirmed that %RSD of each chemical was within 25% limit recommended by United States Environment Protection Agency (US EPA). The result of quality control is shown in Appendix 5.

3. Results

3.1. Review of the chemical components in MSDS

We reviewed MSDS to determine whether the trade secret materials were contained in the products or not. Among a total of 48 products which had information from MSDS, 5 ingredients were contained in one product on average. It was also identified that 45 products contained trade secret materials, and the range was from 1 to 65%. Only 3 products specified all of chemical constituents with Chemical Abstracts Service (CAS) number on MSDS (Table 2).

Table 2. Numerical information on the products including trade secret in this study

Company	No. of Photoresist Product	No. of Products containing Trade secret
A	26	25
B	7	4
C	9	8
D	9	8
Total	51	45

A total of 238 ingredients with multiple counting were identified in MSDS of 48 products and 48.7% of ingredients were counted as a trade secret. When removing multiple counting and trade secret ingredients, 34 chemical ingredients which have CAS number were identified.

Propylene glycol monomethyl ether acetate (PGMEA) was the most used ingredient (33 out of 48 products), followed by in order, cyclohexanone (11 out of 48 products), Propylene glycol monomethyl ether (PGME) (in 7 products) and, 2-Heptanon and Ethyl 3-ethoxypropionate (EEP) (in 7 products) (Table 3). Names and use frequency of other 29 chemical ingredients are shown Appendix 7. Also, trade secret ingredients which do not have CAS number comprised 13 constituents, and it is shown Appendix 8.

At least one of four carcinogens was specified in MSDS of 16 products (33.3%) as shown in Table 4, but some of the corresponding hazardous identification and toxicological information were specified inappropriately in MSDS. Eight products specified accurately hazardous identification and toxicological information in MSDS, 6 products only specified international toxicological information from International Agency for Research on Cancer (IRAC), American Conference of Governmental Industrial Hygienists (ACGIH), Occupational Safety and Health Administration (OHSA), and the domestic information from Ministry of Employment and Labor (MOEL) was not specified. Even 1 product did not specify any toxicological information in MSDS, and 1 out of 16 MSDS of photoresist products was not collected. Cyclohexanone was contained in 11 products with the content from 3 to 40%, and it is usually used with PGMEA and acrylic resin. Ethylbenzene and pyridine were contained in each 1 product (0.1-1%), and 1,4-Dioxane was contained less than 1% in 4 products as an impurity (Table 4).

Table 3. Frequently founded chemical names in MSDS of photoresist products

No.	Constituent	CAS No.	Frequency of usage
1	Trade secret ingredients[1)]	-	116
2	Propylene glycol monomethyl ether acetate	108-65-6	33
3	Cyclohexanone	108-94-1	11
4	Propylene glycol monomethyl ether	107-98-2	7
5	2-Heptanon	110-43-0	7
6	Ethyl 3-ethoxypropionate	763-69-9	7
7	Other ingredients[2)]	-	57
	Total ingredients		238

[1)] Trade secret ingredients are shown Appendix 9.
[2)] Other ingredients are shown Appendix 8.

Table 4. Information on the carcinogens specified in MSDS of photoresist products

Constituent	CAS No.	No. of Products	Content (%)	Korea MOEL[1)]	IARC[2)]	ACGIH[3)]	NTP[4)]	EU CLP[5)]
Cyclohexanone	108-94-1	11	3 – 40	- Carcinogen 2, Skin - TWA : 25 ppm - STEL : 50 ppm	- Group 3	- A3 - Dermal toxicity ('Skin')		
Ethylbenzene	100-41-4	1	0.1 – 1.0	- Carcinogen 2 - TWA : 100 ppm - STEL : 125 ppm	- Group 2B	- A3		
Pyridine	110-86-1	1	0.1 – 1.0	- Carcinogen 2 - TWA : 2 ppm	- Group 3	- A3		
1,4-Dioxane	123-91-1	4	< 1.0	- Carcinogen 2 - Dermal toxicity('Skin') - TWA : 20 ppm	- Group 2B	- A3 - Dermal toxicity ('Skin')	- R	- Carcinogen 2

1) Ministry Of Employment and Labor, Carcinogen classifications – Carcinogen 1A : Have sufficient evidence of carcinogen to human, Carcinogen1B : Have sufficient evidence of carcinogen to animal or limited evidence of carcinogen to human and animal, Carcinogen 2 : Have insufficient evidence of carcinogen to human and animal

2) International Agency for Research on Cancer, Carcinogen classifications – Group 1 : Carcinogenic to humans, Group 2A : Probably carcinogenic to humans, Group2B : Possibly carcinogenic to humans, Group 3 : Not classifiable as to its carcinogenicity to humans, Group 4 : Probably not carcinogenic to humans.

3) American Conference of Governmental Industrial Hygienists, Carcinogen classifications – A1 : Confirmed human carcinogen, A2 : Suspected human carcinogen, A3 : Confirmed animal carcinogen with unknown relevance to humans, A4 : Not classifiable as a human carcinogen, A5 : Not suspected as a human carcinogen.

4) National Toxicology Program, Carcinogen classifications – K : Know to be human carcinogens, R : Reasonable anticipated to be human carcinogens.

5) Classification, Labelling, Packing of substances and mixture, Carcinogen classifications – Carcinogen 1A : Known to have carcinogenic potential humans, Carcinogen 1B : May causes cancer, Carcinogen 2 : Suspected of causing cancer

3.2. Comparison of analytical results with MSDS

As a result of qualitative analysis, 9 ingredients which should not be designated as the trade secrets by KOSHAct were identified with no information in MSDS (Table 5). 5 out of the 9 ingredients of them did not specify its toxicological information in MSDS though required. It contained carcinogens; 1,4-Dioxane and 2-Butoxyethanol, toxic chemical; p-Cresol, 2,3-Dimethylphenol and 3,4-Dimethylphenol, hazardous substances requiring management by KOSHAct; p-Cresol, 1,4-Dioxnae, 2-Butoxyethanol.

According to MSDS, 1,4-Dioxane was listed as an impurity in 4 products, but it was detected only in 1 product. Instead, 1,4-Dioxane was detected in other 7 products, which did not specify any information about 1,4-Dioxane in MSDS. Those 7 products were from one supplier in Korea, and include 2-Heptanone and novolak resin simultaneously. 2-Butoxyethanol was detected in 3 products. All of 3 products were from different suppliers in Korea after 2010 (Table 5).

Table 5. Chemical constituents identified which should not be listed as the trade secrets by Korea Occupational Safety and Health Act but no information on MSDS

Compound	CAS No.	Korea MOEL[1)] TWA (STEL) ppm, CMR	KOSHA[2)]	IARC[3)]	ACGIH[4)]	NCIS[5)]	NTP[6)]	EU CLP[7)]
Ethylbenzene	100-41-4	- 100 (125), Car. 2	- Hazardous substances requiring management	- Group 2B	- A3			
p-Cresol *	106-44-5	- 5 - Dermal toxicity('Skin')	- Hazardous substances requiring management		- A4 - Dermal toxicity('Skin')	- Toxic chemical (91-1-268)		
1,3-Dimethylbenzene	108-38-3	- 100 (150)		- Group 3	- A4	- Toxic chemical (97-1-275)		
1,4-Dioxane *	123-91-1	- 20, Car. 2 - Dermal toxicity('Skin')	- Hazardous substances requiring management	- Group 2B	- A3 - Dermal toxicity('Skin')		- R	- Car. 2
2,3-Dimethylphenol *	526-75-0					- Toxic chemical (97-1-274)		
3,4-Dimethylphenol *	95-65-8					- Toxic chemical (97-1-274)		
Styrene	100-42-5	- 20 (40), Car. 2	- Hazardous substances requiring management	- Group 2B	- A4		- R	
2-Butoxyethanol *	111-76-2	- 20, Car. 2 - Dermal toxicity('Skin')	- Hazardous substances requiring management	- Group 3				
2-Heptanone	110-43-0		- Hazardous substances requiring management					

1) Ministry Of Employment and Labor, Carcinogen classifications – Carcinogen 1A : Have sufficient evidence of carcinogen to human, Carcinogen 1B : Have sufficient evidence of carcinogen to animal or limited evidence of carcinogen to human and animal, Carcinogen 2 : Have insufficient evidence of carcinogen to human and animal
2) Korea Occupational Safety and Health Agency – Hazardous substances requiring management should not be designated as the trade secret by KOSHAct
3) International Agency for Research on Cancer, Carcinogen classifications – Group 1 : Carcinogenic to humans, Group 2A : Probably carcinogenic to humans, Group 2B : Possibly carcinogenic to humans, Group 3 : Not classifiable as to its carcinogenicity to humans, Group 4 : Probably not carcinogenic to humans.
4) American Conference of Governmental Industrial Hygienists, Carcinogen classifications – A1 : Confirmed human carcinogen, A2 : Suspected human carcinogen, A3 : Confirmed animal carcinogen with unknown relevance to humans, A4 : Not classifiable as a human carcinogen, A5 : Not suspected as a human carcinogen.
5) National Chemicals Information System in Korea– Toxic chemical should not be designated as the trade secret by KOSHAct
6) National Toxicology Program, Carcinogen classifications – K : Know to be human carcinogens, R : Reasonable anticipated to be human carcinogens.
7) Classification, Labelling, Packing of substances and mixture, Carcinogen classifications – Carcinogen 1A : Known to have carcinogenic potential humans, Carcinogen 1B : May causes cancer, Carcinogen 2 : Suspected of causing cancer
* Toxicological information of those ingredients were not specified in MSDS

Quantitative analysis was conducted for 21 chemicals (Appendix 6). Target chemicals were selected based on 2 criteria: Firstly, we selected VOC compounds specified in MSDS, and secondly, we selected VOC compounds identified by qualitative analysis which should not be designated as trade secret by KOSHAct. Among 21 chemicals, 19 chemicals (90.4%) were quantitated, and the frequency detected the range from 1 to 36. The sum of detected chemicals was 141. On the basis of the result of quantitative analysis, we compared the analytical result with MSDS. A total of 89 out of 141 ingredients were in accordance with MSDS and the comparison results between analytical result and MSDS data were different according to the type of solvent used (CS_2 vs. Methanol). In samples diluted with CS_2, the content of 46 out of 89 ingredients (51.7%) was within the range recorded in MSDS. It is corresponded with MSDS, and the content of 14 ingredients (15.7%) was within the range of ± 5%. The content of 29 ingredients (32.6%) exceeded the range of ± 5%, and the content of 14 ingredients (15.7%) were over the range of ± 10%. In the case of samples diluted with methanol, the content of 55 out of 89 ingredients (61.8%) was within in the range specified in MSDS, thus it is corresponded with MSDS. The content of 16 ingredients (18.0%) was within the range of ± 5%, the content of 18 ingredients (20.2%) exceeded the range of ± 5%, and the content of 9 ingredients was over the range of ± 10% (Table 6).

As the products, the number of 20 out of 48 products (41.7%) corresponded within the range of ± of 5%, the number of 28 out of 48 products (58.3%)

exceeded the range of ± 5%, and 15 products (31.3%) were over the range of ± 10% (Table 7). Appendix 10 and 11 show an example of chemical constituent and content comparison between MSDS and the analytical result.

Table 6. Comparison of ingredient content between MSDS and analytical result

	No. of Ingredient diluted with CS_2	No. of Ingredient diluted with Methanol
Accordance with MSDS	46 (51.7%)	55 (61.8%)
The range of ± 5%	14 (15.7%)	16 (18.0%)
The range of ± 5 - 10%	15 (16.9%)	9 (10.1%)
Over the range of ± 10%	14 (15.7%)	9 (10.1%)
Total	89 (100.0%)	89 (100.0%)

- According to KOSHAct, content of the chemical composition information could be specified its range from the lowest to the highest, and the lowest and highest content must be in range of ± 5% of real content. Also, if the content is lower than 5%, its lowest content must be specified over than 1%; Carcinogen and Mutagen must be specified over than 0.1%, and Reproductive toxicant must be specified over than 0.3%.

Table 7. The accordance rates between in MSDS and analytical results

	No. of Product
The range of ± 5%	20 (41.7%)
The range of ± 5 - 10%	13 (27.1%)
Over the range of ± 10%	15 (31.3%)
Total	48 (100.0%)

- According to KOSHAct, content of the chemical composition information could be specified its range from the lowest to the highest, and the lowest and highest content must be in range of ± 5% of real content. Also, if the content is lower than 5%, its lowest content must be specified over than 1%; Carcinogen and Mutagen must be specified over than 0.1%, and Reproductive toxicant must be specified over than 0.3%.

3.3. The volatile organic compounds emitted from the photoresist after heat treatment

A total of 51 products were analyzed by SPME-GC/MS for its by-products resulted from heat treatment. As a result of analysis, 129 chemicals classified according to CAS No. were identified, and all of them were not specified in MSDS. Toluene was the most released chemical (29 out of 51 products), followed by in order, p-Cresol (23 out of 51 products), PGME (22 out of 51 products), and Acetone (18 out of 51 products). Appendix 12 shows the chemicals which detected over 10 out of total 51 products.

As an analytical result, 17 out of 129 chemicals (13.2%) were CMRs, 13 out of 17 CMRs (72.2%) were classified as a carcinogen 2 by the MOEL (Table 9). Toluene was detected 29 out of 51 products (56.9%), methyl isobutyl ketone (MIBK) and 1,4-Dioxane were released from 13 products (25.5%), respectively. Benzene classified as a carcinogen by several governmental or academic agencies, was detected from 9 products (17.6%). In addition, aromatic compound such as styrene, ethylbenzene and chlorobenzene were detected. Figure 2 shows a typical example of HS/SPME-GC/MS chromatogram. Hazardous chemicals such as benzene, MIBK, and toluene were released from photoresist products.

According to the MSDS, phenolic resin (novolak) was the most used resin (41.2%), following by in order, acrylic resin (27.5%) and polystyrene resin (3.9%). Resin type was unknown in 27.5% (Figure 3). Twenty-one products including novolak resin were analyzed to determine whether the formaldehyde emission from novolak resin in the actual working temperature. Fourteen products including acrylic resin were also analyzed to compare with novolak resin. Formaldehyde was emitted from 12 out of 21 products including novolak resin, which contained 2-heptanone and gamma-butyrolactone simultaneously; 14 products including acrylic resin did not release formaldehyde. In addition, p-Cresol was also released from 90% of products including novolak resin.

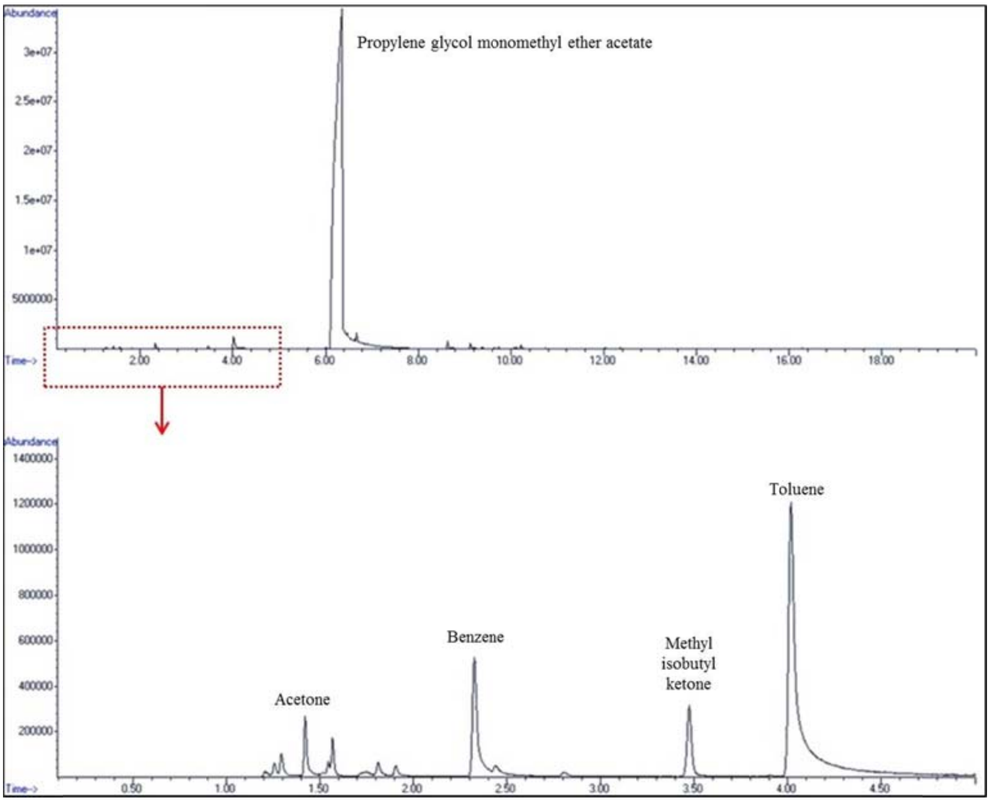

Figure 2. An example of volatile organic compounds emitted after heating by HS/SPME-GC/MS.

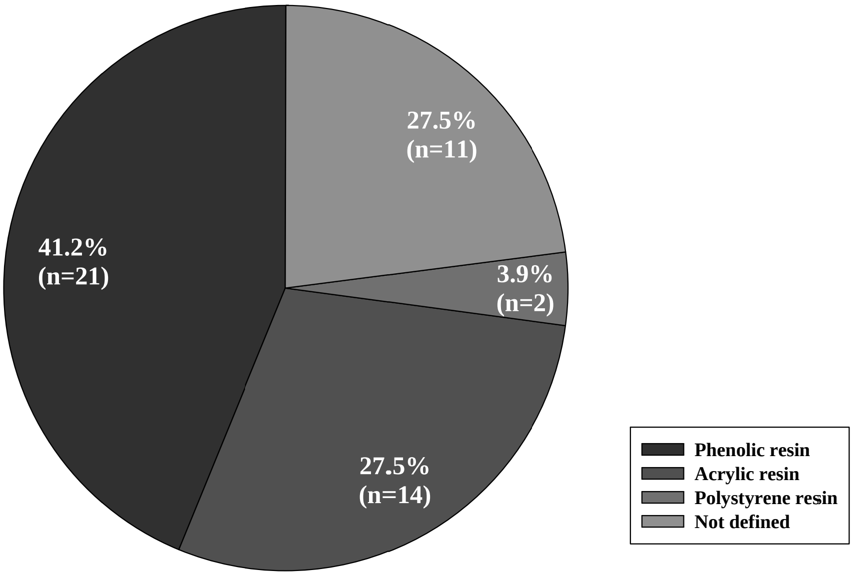

Figure 3. Categorization in relation to resin type.

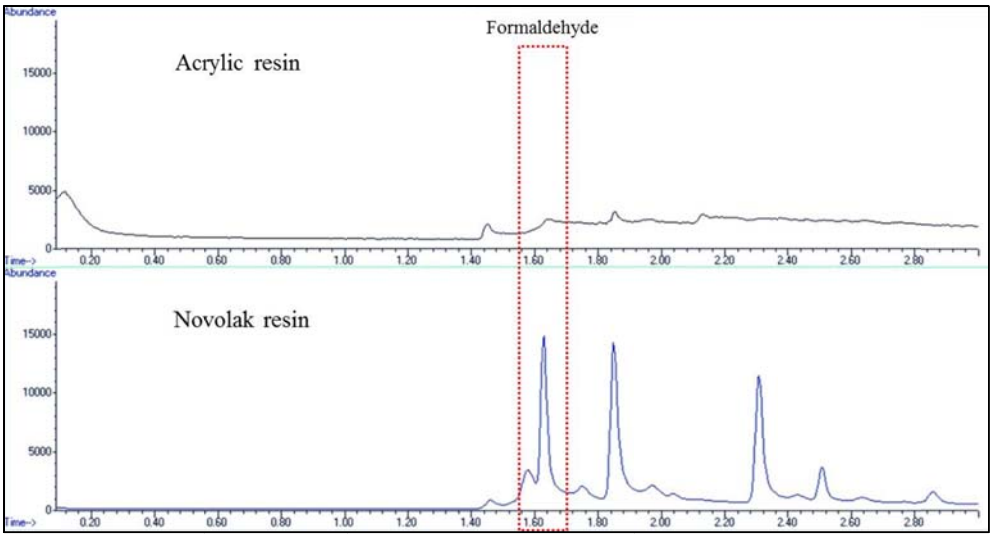

Figure 4. An example of HS/SPME-GC/MS chromatogram for formaldehyde by resin types.

Table 8. The information of the CMRs detected from HS-SPME/GC-MS

Compound	CAS No.	No. of products	Korea MOEL[1]		Carcinogenicity			
			TWA(STEL), ppm	CMR	IARC[2]	ACGIH[3]	NTP[4]	EU CLP[5]
Toluene	108-88-3	29 (56.9%)	- 50 (150)	- Repr. 2	- Group 3	- A4		
Methyl isobutyl ketone	108-10-1	13 (25.5%)	- 50 (75)	- Car. 2	- Group 2B	- A3		
1,4-Dioxane	123-91-1	13 (25.5%)	- 20	- Car. 2	- Group 2B	- A3	- R	- Car. 2
Benzene	71-43-2	9 (17.6%)	- 1 (5)	- Car. 1A, Mut. 1B	- Group 1	- A1	- K	- Car. 1A
Styrene	100-42-5	5 (9.8%)	- 20 (40)	- Car. 2	- Group 2B	- A4	- R	
Chlorobenzene	108-90-7	4 (7.8%)	- 10 (20)	- Car. 2		- A3		
Ethylbenzene	100-41-4	3 (5.9%)	- 100 (125)	- Car. 2	- Group 2B	- A3		
Cyclohexanone	108-94-1	3 (5.9%)	- 25 (50)	- Car. 2	- Group 3	- A3		
2-Butoxyethanol	111-76-2	3 (5.9%)	- 20	- Car. 2	- Group 3			
Chloroform	67-66-3	3 (5.9%)	- 10	- Car. 2	- Group 2B	- A3	- R	- Car. 2
2-Butoxyethyl acetate	112-07-2	2 (3.9%)	- 20	- Car. 2		- A3		
Naphthalene	91-20-3	2 (3.9%)	- 10 (15)	- Car. 2	- Group 2B	- A3	- R	- Car. 2
1,4-Dichlorobenzene	106-46-7	1 (2.0%)	- 10 (20)	- Car. 2	- Group 2B	- A3	- R	- Car. 2
Phenol	108-95-2	1 (2.0%)	- 5	- Mut. 2	- Group 3			
Hexane	110-54-3	1 (2.0%)	- 50	- Rep. 2				
Dichloromethane	75-09-2	1 (2.0%)	- 50	- Car. 2	- Group 2B	- A3	- R	- Car. 2
Cumene	98-82-8	1 (2.0%)	- 50	- Car. 2	- Group 2B			

[1] Ministry Of Employment and Labor, Carcinogen classifications – Carcinogen 1A : Have sufficient evidence of carcinogen to human, Carcinogen1B : Have sufficient evidence of carcinogen to animal or limited evidence of carcinogen to human and animal, Carcinogen 2 : Have insufficient evidence of carcinogen to human and animal

[2] International Agency for Research on Cancer, Carcinogen classifications – Group 1 : Carcinogenic to humans, Group 2A : Probably carcinogenic to humans, Group2B : Possibly carcinogenic to humans, Group 3 : Not classifiable as to its carcinogenicity to humans, Group 4 : Probably not carcinogenic to humans.

[3] American Conference of Governmental Industrial Hygienists, Carcinogen classifications – A1 : Confirmed human carcinogen, A2 : Suspected human carcinogen, A3 : Confirmed animal carcinogen with unknown relevance to humans, A4 : Not classifiable as a human carcinogen, A5 : Not suspected as a human carcinogen.

[4] National Toxicology Program, Carcinogen classifications – K : Know to be human carcinogens, R : Reasonable anticipated to be human carcinogens.

[5] Classification, Labelling, Packing of substances and mixture, Carcinogen classifications – Carcinogen 1A : Known to have carcinogenic potential humans, Carcinogen 1B : May causes cancer, Carcinogen 2 : Suspected of causing cancer

4. Discussion

We identified the chemical constituents in the photoresists and their possible by-products during process, and then compared the analytical result with the MSDS data in this study. We found that not only some photoresist products have contained toxic chemicals but also their by-products could be formed in the conditions of actual process. Even some constituents were not specified in MSDS comparing with the analytical results.

Firstly, we reviewed MSDS to acquire the basic information such as supplier, revision date, chemical constituent and toxicity. A total of 238 ingredients with multiple counting (35 ingredients removing multiple counting) were used, and half of them were listed as a trade secret. Appendix 8 shows that trade secret ingredients were specified in various terms. Furthermore some ingredients consisted of similar component. For instance, the high-molecular compound which is used for determining the mechanical property was specified in different terms such as resin, polymer and monomer. Also, the ingredients which control a photochemical reaction during exposure to light called with various name like sensitizer, photoactive, initiator and generator (Van Zant, 2004, Park et al., 2011). Thus, it needs to unify the names of individual ingredient for systematic management. Also, we suggest that resin type should be informed in MSDS at least because previous study (Park et al., 2011) has shown that novolak resin could release aromatic compound such as benzene, toluene, phenol, and cresol through thermal energy. In this study, 8 products informed the CAS No. of resin (Appendix 7), and 37 products informed the type of resin (Appendix 9).

PGME and PGMEA were the most used in this study instead of ethylene glycol ether derivatives (EGME, EGMEA, EGEE, EGEEA), and those were contained in 33 and 7 products, respectively (Table 3). It is known that PGME and PGMEA have been substituted for ethylene glycol methyl ether (EGME), ethylene glycol methyl ether acetate (EGMEA), ethylene glycol ethyl ether (EGEE), ethylene glycol ethyl ether acetate (EGEEA), those which seem to correlate with reproductive toxicant (Chelton et al. 1991, Hallock et al. 1995). Although propylene glycol ether derivatives (PGME, PGMEA) have a lower toxicity than ethylene glycol ether derivatives (EGME, EGMEA, EGEE, EGEEA) and seem to have low deleterious effects, there were not enough references to substantiate that PGME and PGMEA are entirely safe, and thus it should be handled with caution (Multigner et al.,2005).

According to the result of MSDS review of 48 products, 4 carcinogens were included in photoresist; cyclohexanone, ethylbenzene, pyridine and 1,4-dioxane. Cyclohexanone were contained in 11 products, over than 80% of products was provided after 2010. All products including cyclohexanone contained PGMEA simultaneously, and those were not used with novolak resin. We assume that cyclohexanone is not essential chemical in photoresist because it is not all products including PGMEA contained cyclohexanone, thus we recommend restriction the usage of cyclohexanone or substitution of low toxic chemicals for cyclohexanone. In 4 products, 1,4-dioxane was contained as an impurity, ethylbenzene and pyridine was used in 2 products, respectively. However, it was not to refer to toxicological information in MSDS, thus it is difficult to make a decision about its harmfulness using MSDS. Furthermore, 4 products including cyclohexanone did not specify its hazardous identification in MSDS; according to MOEL, if the content of carcinogen 2 in the products is over than 1%, the product is considered as a carcinogen 2. Cyclohexanone is classified as a carcinogen 2 by MOEL and the content is from 3- 40% in 11 products (Table 4), thus it is recommended that the standard of MOEL should be specified in MSDS.

As shown in Table 5, we confirmed that hazardous chemicals were included in photoresist products. 1,4-Dioxane classified as carcinogen 2 by MOEL and EU CLP, and group 2B by IARC was detected in 8 products; one product informed it as an impurity. Seven products did not specify whether or not 1,4-dioxane is present. All products including 1,4-Dioxane contained 2-Heptanone and novolak resin simultaneously. We assume that there is a possibility of 1,4-dioxane exposure from the use of the products, including 2-Heptanone and novolak resin simultaneously. As an analytical result, most of the products did not specify the information of impurity, although it is used as an impurity, toxicological information should be indicated. Also, 2-Butoxyethanol (EGBE) classified as carcinogen 2 by MOEL was detected in 3 products, but any information was not specified in MSDS. Previous studies have shown that EGBE has a haemolytic and foetotoxic effects, also seems to form a tumor (Multigner et al., 2005). According to the KOSHAct, 1,4-dioxane and EGBE should not to be listed as a trade secret due to its toxicity because they are classified hazardous substances requiring management by KOSHA, thus their toxicity should be specified in MSDS. P-cresol, 2,3-dimethylphenol and 3,4-dimethylphenol are categorized as toxic chemicals by National Chemicals Information System (NCIS), and the information of those chemicals should be specified in MSDS; according to KOSHAct, chemicals which are classified as a toxic chemical by NCIS should not be designated as a trade secret. Also, we assume that p-cresol, 2,3-dimethylphenol and 3,4-dimethylphenol seem to be the form of novolak resin. As we already mentioned above, resin type should be specified in MSDS due to the possibility that novolak resin may contain hazardous chemicals (Park et al., 2011).

After qualitative analysis, quantitative analysis was performed for CMRs and toxic materials (Appendix 6). Table 6 shows that the analytical result was different according to dilution solvent because each chemical has a different solubility in each solvent. Accordingly, when analyzing constituents of an unknown sample, crossover analysis should be performed using solvents which have different characteristics.

On the base of qualitative evaluation, we compared the chemical contents between MSDS and the result of GS/FID. The analytical result shows that only 41.7% of total products were within the range of ± 5%, and over 30% of products exceeded over the range of ± 10% (Table 7). Likewise, previous studies have shown that the agreement rates with MSDS and the analytical result had an overall low level (Chung et al., 2001, Lee et al., 2003, Lee et al., 2004, Lee et al., 2009, Hong et al., 2013).

We performed the analysis of by-products along with the analysis of diluted sample. According to a US patent, volatile compounds, such as benzene and phenyl sulfide, could be released from photoresist products as the by-product. In addition, there is analytical result of thermal decomposition experiment which detected aromatic compounds such as benzene, toluene and cresol, but the temperature condition was higher than the operative temperature (Goodner, 2008, Park et al., 2011). Hence, we performed analysis at 110 ℃ in accordance with operative temperature; soft bake for 70 - 90 ℃, hard bake for 120 - 135 ℃ (Wald et al., 1987, Park et al., 2011). Table 8 shows that various chemical compounds were released as the by-product at actual operative temperature. In this study, benzene which is known to induce leukemia was detected in 9 products. In over 50% of the total product, toluene was detected, which has respect to reproductive toxicant. Furthermore, 1,4-dioxane added as an impurity was detected in 14 products and 4 products were specified the information of impurity in MSDS. As a previous researcher reported that formaldehyde - which is classified as Group 1 and a known human carcinogen - could be released from novolak resin by high temperature or press (Park et al., 2011). For this reason analysis was conducted to determine the formaldehyde emission from novolak resin. Firstly, we conducted the analysis at the same temperature with VOSs method (110 ℃), but the formaldehyde peak was not detected. Thus, analysis was conducted at 3 different temperatures: 110, 150 and, 180 ℃ with the same product (Appendix 13). In the analytical result, formaldehyde was detected in 12 out of 21 products (57.1%). The products which detected the highest peak included 2-Heptanone and gamma-butyrolactone identically. Both products were provided by one supplier from Korea. We verified that photoresist products generate hazardous by-products at an operative temperature. As the legal regulation associated with the by-product is not yet established, by-products have not been controlled by the legal regulation in Korea. However, as there is potential emission of hazardous chemicals in Fab process, there should be consideration for managing of the potential emission.

Limitations of this study were that it was hard to collect MSDS of all product and we only analyzed VOCs. Moreover, there are different results according to the dilution solvent (Appendix 10, 11), so we assume that there is a need to select the solvent differently for each target chemical or perform crossover analysis using solvents which have different characteristics. Also, it was hard to adjust UV light during the analysis of the by-product. Therefore, further studies require analysis of macromolecule in photoresist products, considering the dilution solvent and UV light.

This study serves useful information to manage chemicals used in fabrication process as identification of the constituents of photoresist products and their by-products. The result of comparison between MSDS and analysis result has shown that it needs to reexamine MSDS. Also, diversified management suited to each process is necessary because exposure rate vary by the process characteristics.

5. Conclusions

In this study, we identified a total of 51 photoresist products and their by-products. Samples were collected with MSDS from 3 companies and 1 academic semiconductor research center in Korea. Firstly, we reviewed MSDS, and secondly, chemical constituents were identified through a qualitative and quantitative method. Lastly, a qualitative analysis of possible by-products was simultaneously performed at operative temperature.

- Photoresist products contained various chemicals, and some were harmful to human. Also the chemicals information was not specified correctly in MSDS.
- In the result of analysis, hazardous chemicals were detected and not specified in MSDS. Furthermore, chemical constituents were not matched with MSDS data and the analytical result.
- CMRs including benzene were released as by-products at operative temperature, and formaldehyde and p-cresol were also released from some products containing novolak resin.

Therefore, it is needed to manage systematically, and reexamine chemicals used in fabrication process and their MSDS. Also, when we manage working environment, should recognize the risk of exposure to possible by-products.

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국문초록

반도체 제조 공정에서 사용하는 포토레지스트의 성분 및 발생 가능한 부산물 분석

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연구목적 : 반도체 산업에서는 다양한 화학물질을 사용하고 있으나 해당 산업의 기밀성과 폐쇄성으로 노출자료와 공정정보에 대해 알려진 것은 소수에 불과하다. 특히 웨이퍼 가공 공정의 포토 공정에서 사용되는 포토레지스트 제품에는 다양한 유기용매와 영업비밀물질들이 포함되어 있는 것으로 알려져 있다. 실제 공정에서 사용되는 화학물질에 대한 유해위험성 정보는 주로 물질안전보건자료를 통해 확인되고 있으나, 영업비밀물질과 같은 미지의 성분 정보는 알 수 없으므로 이러한 성분에 대한 확인이 필요한 실정이다. 따라서 본 연구의 목적은 반도체 제조 공정에서 사용하는 포토레지스트를 정성·정량적 방법으로 평가하여 물질안전보건자료와 비교하고, 더불어 2차적으로 발생 가능한 부산물의 성분을 분

석하는 것이다.

연구방법 : 세 곳의 사업장 및 하나의 반도체 연구소에서 수거된 총 51개의 포토레지스트와 48개의 물질안전보건자료를 대상으로 분석을 진행하였다. 분석은 크게 원액 분석과 2차 부산물 분석으로 이루어져있다. 원액 분석은 이황화탄소와 메탄올로 제품을 100배 희석하여 질량분석기와 불꽃이온화검출기가 장착된 가스크로마토그래피를 이용하여 분석 하였으며, 분석결과와 물질안전보건자료의 기재 내용을 비교하여 영업비밀 제외 대상물질의 포함 여부를 알고자 하였다. 또한 실제 작업 시 발생 가능한 부산물의 성분을 분석하기 위해 제품 원액을 고체상미량분석법을 이용하여 분석을 진행하였다.

연구결과 : 총 51개의 제품 중 45개의 제품에 영업비밀물질이 1-65%의 함량으로 포함되어 있었다. 물질안전보건자료를 보유한 48개의 제품은 238개의 성분으로 이루어졌고, 이 중 48.7% 성분이 카스번호가 부여되지 않은 영업비밀물질로 이루어져있었다. 정성분석 결과 9개 화학물질이 검출되었으며 이 중 5개 화학물질의 독성 정보가 물질안전보건자료에 누락되어 있었다. 정량분석은 정성분석에서 검출된 물질 중 물질안전보건자료에 기재되거나, 영업비밀제외대상물질 중 물질안전보건자료에 기재되지 않은 물질을 대상으로 하였다. 선행연구의 결과에 의하면 구성성분과 MSDS 기재 내용의 일치율이 낮은 결과를 보였으며, 본 연구에서도 전체적인 제품 분석 결과와 물질안전보건자료의 기재 내용은 41.7%의 낮은 일치율을 보였다. 제품 원액을 대상으로 한 2차 부산물 분석에

서 벤젠과 포름알데히드와 같이 발암성이 높은 물질들이 검출되었다.

결론 : 본 연구에서 물질안전보건자료의 기재 성분과 포토레지스트의 실제 성분에 차이가 있으며, 상당량이 영업비밀물질로 표기되어 있음을 알 수 있었다. 따라서, 화학물질의 체계적인 관리 및 MSDS의 재검토가 요구된다. 또한 공정 온도조건에서 벤젠이나 포름알데히드와 같이 제품에 포함 되지 않은 휘발성 유기화합물이 2차 부산물로 발생할 가능성이 있으므로, 작업환경관리 시 이를 고려하여 각 작업 공정에 알맞은 대책을 수립할 필요가 있다.

주요어: 반도체 산업, 포토공정, 포토레지스트, 2차 부산물, 영업비밀물질, 물질안전보건자료, 고체상미량분석법

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Appendix

Appendix 1. The conditions of GC/MS for analysis of bulk sample

Variables	Conditions
Instrument	Gas chromatography - Mass spectrometer (7890A – 5975C, Agilent Technology, USA)
Injector	Auto-sampler (PAL COMBI-xt, Switzerland)
Inlet Temperature	260 ℃
Injector volume	1 μl
Split ratio	50:1
Column	DB-5MS (30 m x 0.25 mm x 0.25 μm, Agilent, USA)
Carrier gas	Helium (99.99% purity), 1 ml/min
Column Temperature	40 ℃(3 min) → 10 ℃/min, 250 ℃ → 250 ℃(2 min)
Detector Temperature	280 ℃
MS Quad / Source	150 ℃ / 250 ℃
Scan range	35 – 300 m/z

Appendix 2. The conditions of GC/FID for analysis of bulk sample

Variables	Conditions
Instrument	Gas chromatography – Flame ionization detector (6890N, Agilent Technology, USA)
Injector	Auto-sampler (7683B Series, Agilent Technology, USA)
Inlet Temperature	260 ℃
Injector volume	1 μl
Split ratio	50:1
Column	DB-5 (30 m x 0.25 mm x 0.25 μm, Agilent, USA)
Carrier gas	Helium (99.99% purity), 1 ml/min
Column Temperature	40 ℃(3 min) → 10 ℃/min, 250 ℃ → 250 ℃(2 min)
Detector Temperature	280 ℃

Appendix 3. The conditions of HP/SPME-GC/MS for analysis of VOCs

Variables	Conditions
Instrument	Gas chromatography - Mass spectrometer (7890A – 5975C, Agilent Technology, USA)
Injector	Auto-sampler (PAL COMBI-xt, Switzerland)
Inlet Temperature	250 ℃
Injector volume	1 μl
Split ratio	30:1
Column	DB-5MS (30 m x 0.25 mm x 0.25 μm, Agilent, USA)
Carrier gas	Helium (99.99% purity), 1 ml/min
Column Temperature	40 ℃(3 min) → 10 ℃/min, 250 ℃ → 250 ℃(2 min)
Detector Temperature	260 ℃
MS Quad / Source	150 ℃ / 250 ℃
Scan range	35 – 225 m/z

Appendix 4. The conditions of HP/SPME-GC/MS for analysis of formaldehyde

Variables	Conditions
Instrument	Gas chromatography - Mass spectrometer (7890A – 5975C, Agilent Technology, USA)
Injector	Auto-sampler (PAL COMBI-xt, Switzerland)
Inlet Temperature	200 ℃
Injector volume	1 μl
Split ratio	30:1
Column	DB-WAX (30 m x 0.25 mm x 0.25 μm, Agilent, USA)
Carrier gas	Helium (99.99% purity), 1ml/min
Column Temperature	35 ℃(5 min) → 10 ℃/min, 180 ℃
Mode	SIM mode (m/z: 29, 30)
Detector Temperature	210 ℃
MS Quad / Source	150 ℃ / 250 ℃
Scan range	35 – 225 m/z

Appendix 5. The result of quality control

No.	Target Chemical substance	RT[1)] (min)	Reproducibility (% RSD[2)])	
			Before analysis	After analysis
1	Propylene glycol monomethyl ether	4.4	7.26	6.61
2	1,4-Dioxane	4.9	1.34	2.89
3	Ethylbenzene	7.9	1.00	2.88
4	Propylene glycol monomethyl ether acetate	8.1	1.12	3.13
5	2-Heptanone	8.5	0.74	2.94
6	Cyclohexanone	8.6	0.92	2.91
7	Ethyl 3-ethoxypropionate	10.3	1.20	3.16

1) Retention time
2) Relative standard deviation; (standard deviation/average) x 100 (%)

Appendix 6. Target chemicals for quantitative analysis

No.	Compound[1)]	CAS No.
1	Ethylbenzene	100-41-4
2	Styrene	100-42-5
3	p-Cresol	106-44-5
4	Propylene glycol monomethyl ether	107-98-2
5	m-Xylene	108-38-3
6	Propylene glycol monomethyl ether acetate	108-65-6
7	Cyclohexanone	108-94-1
8	2-Heptanone	110-43-0
9	Pyridine	110-86-1
10	2-Butoxyethanol	111-76-2
11	Butyl acetate	123-86-4
12	1,4-Dioxane	123-91-1
13	2-(2-Butoxyethoxy)ethly acetate	124-17-4
15	Methyl 3-methoxypropanoate	3852-09-03
16	3-methoxybutyl acetate	4435-53-4
17	2,3-Dimethylphenol	526-75-0
18	Ethyl-(s)-lactate	687-47-8
19	Ethyl 3-ethoxypropionate	763-69-9
20	3,4-Dimethylphenol	95-65-8
21	Gamma-butyrolactone	96-48-0

[1)] Target compounds, which contained in products or have a hazard to human, were selected for quantitative analysis.

Appendix 7. Other ingredient according to Table 3

NO.	Constituent	CAS No.	Number of use
1	Ethyl lactate	97-64-3	5
2	n-Butyl acetate	123-86-4	4
3	Methyl 3-methoxypropanoate	3852-09-03	4
4	3-methoxybutyl acetate	4435-53-4	4
5	Diethylene glycol ethyl methyl ether	1002-67-1	3
6	1,3,5-triazine-2,4,6-triamine, polymer with formaldehyde, methylated	68002-20-0	3
7	Ethyl-(s)-lactate	687-47-8	3
8	Novolak resin *	9003-35-4	3
9	Gamma-butyrolactone	96-48-0	4
10	Carbon black	1333-86-4	2
11	Novolac (o-Cresol, formaldehyde, epichlorohydrin polymer) *	29690-82-2	2
12	Dipropylenegylcolmethylether	34590-94-8	2
13	Novolac (Formaldehyde, polymer with dimethylphenol and methylphenol) *	9065-82-1	2
14	Ethylbenzene	100-41-4	1
15	Photoactive compound	107761-81-9	1
16	Pyridine	110-86-1	1
17	Formaldehyde-dimethylphenol-3-methylphenol-4-methylphenol polymer	117520-84-0	1
18	1,4-Dioxan	123-91-1	1
19	2-(2-Butoxyethoxy)ethly acetate	124-17-4	1
20	Xylene	1330-20-7	1
21	C.I. Pigment Blue 15:6	147-14-8	1
22	2-Methoxy-1-propanol	1589-47-5	1
23	Multi functional acrylic monomer	29570-58-9	1
24	Pigment Red	4051-63-2	1
25	Propyleneglycol monoethylether	52125-53-8	1
26	C.I. Pigment violete 23	6358-30-1	1
27	Acrylic resin *	65697-21-4	1
28	2,3,4-Trihydroxybesophenone 2,1,5-diazohaphthoquinone sulfonate	68510-93-0	1
29	2-Butanol	78-92-2	1
	Total ingredients		57

* Products informed the CAS No. of resin.

Appendix 8. Trade secret ingredients according to Table 3

No.	Constituent[1)]	Number of use
1	Resin	36
2	Sensitizer	21
3	Pigment	16
4	Additive	13
5	Monomer	9
6	Derivatives	6
7	Photoactive	4
8	Polymer	3
9	Cross-linker	2
10	Initiator	2
11	Trade secret	2
12	Generator	1
13	Others	1
Total trade secret ingredients		116

[1)] The ingredients which were not specified CAS No. were regarded as trade secret ingredient.

Appendix 9. Numerical information on the products in relation to resin type

Company	No. of photoresist Products	No. of Products classified by resin type			
		Phenolic resin[1)]	Acrylic resin	Polystyrene resin	Other[2)]
A	26	12	5	0	9
B	7	5	0	0	2
C	9	1	6	0	2
D	9	3	3	2	1
Total	51	21	14	2	14

[1)] Phenolic resin consists of phenol-formaldehyde, and it also named novolak resin.

[2)] Resin type was not specified in 11 products, and MSDS of 3 products were not collected

Appendix 10. An example of chemical content comparison between MSDS and the analytical result

No.	Compound	CAS No.	Content in MSDS (%)	Analytical content (%)	
				Diluted with CS_2	Diluted with Methanol
1	2-Heptanon	110-43-0	40-50	33.49	44.14
	Ethyl-(s)-lactate	687-47-8	10-20	10.48	12.74
	p-Cresol *	106-44-5		2.20	2.40
	1,4-Dioxane *	123-91-1		0.25	0.27
2	3-Methoxybutyl acetate	4435-53-4	45-55	72.28	70.55
	Propylene glycol monomethyl ether acetate	108-65-6	10-20	12.90	13.47
	Cyclohexanone	108-94-1	10-20	11.95	14.12
	n-Butyl acetate	123-86-4	<5	1.52	1.38
3	2-Heptanon	110-43-0	77-83	65.66	64.54
	1,4-Dioxane *	123-91-1		0.41	0.34
	p-Cresol *	106-44-5		1.11	0.80
	Gamma-butyrolactone *	96-48-0		3.01	2.86

* p-Cresol, 1,4-Dioxane and gamma-butyrolactone do not specify in MSDS.

Appendix 11. An example of chemical constituent comparison between MSDS and the analytical result

NO.	MSDS		Diluted with CS_2		Diluted with Methanol	
	Compound	CAS No.	Compound	CAS No.	Compound	CAS No.
1	2-Heptanon	110-43-0	2-Heptanon	110-43-0	2-Heptanon	110-43-0
	Ethyl-(s)-Lactate	687-47-8	Ethyl-(s)-Lactate	687-47-8	Ethyl-(s)-Lactate	687-47-8
	Novolak resin	Trade secret				
	Sensitizer	Trade secret				
			1,4-Dioxane	123-91-1	2-methoxy-2-Heptene	61142-43-6
			Benzenemethanol	100-51-6	Benzenemethanol	100-51-6
			Cyclododecane	294-62-2	Cyclododecane	294-62-2
			1,3-Dihydro-3,3,7-trimethyl-5-amino-2H-indol-2-one	998155-19-5	1,3-Dihydro-3,3,7-trimethyl-5-amino-2H-indol-2-one	998155-19-5
			anti-10-hydroxy-5,6,8,9-tetrahydro-5,9-methano-7H-benzocyclohepten-7-one	55139-53-2	Anti-10-hydroxy-5,6,8,9-tetrahydro-5,9-methano-7H-benzocyclohepten-7-one	55139-53-2
			2,2'-methylenebis[4-methyl-Phenol	3236-63-3	2,2'-methylenebis[4-methyl-Phenol	3236-63-3
			2-(1-methylethyl)-9H-Thioxanthen-9-one	5495-84-1	Dodecyl acrylate	2156-97-0
2	Propylene glycol monomethyl ether acetate	108-65-6	Propylene glycol monomethyl ether acetate	108-65-6	Propylene glycol monomethyl ether acetate	108-65-6
	Ethyl-3-ethoxy propionate	763-69-9	Ethyl-3-ethoxy propionate	763-69-9	Ethyl-3-ethoxy propionate	763-69-9
	Propylene glycol monomethyl ether	107-98-2	Propylene glycol monomethyl ether	107-98-2	Propylene glycol monomethyl ether	107-98-2
	Resin	Trade secret				
	Pigment	Trade secret				
	Addictive	Trade secret				
			2-Butoxyethanol	111-76-2	2-Butoxyethanol	111-76-2
			Heptanonitrile	629-08-3	Heptanonitrile	629-08-3
			Cyclododecane	294-62-2	Cyclododecane	294-62-2
			2-Propenoic acid, pentadecyl ester	43080-23-5	Acrylic acid tetradecanyl ester	21643-42-5

NO.	MSDS		Diluted with CS_2		Diluted with Methanol	
	Compound	CAS No.	Compound	CAS No.	Compound	CAS No.
3	2-Heptanon	110-43-0	2-Heptanon	110-43-0	2-Heptanon	110-43-0
	Novolak resin	Trade secret				
	Sensitizer	Trade secret				
			1,4-Dioxane	123-91-1	1,4-Dioxane	123-91-1
			5-methyl-2-hexanone	110-12-3	5-methyl-2-hexanone	110-12-3
			Gamma-butyrolactone	96-48-0	Gamma-butyrolactone	96-48-0
			Butylethylacetaldehyde	123-05-7	2-ethyl-hexanal	123-05-7
			Benzenemethanol	100-51-6	Benzenemethanol	100-51-6
			4,4'-cyclohexylidenebis-Phenol	843-55-0	4,4'-cyclohexylidenebis-Phenol	843-55-0
					2-Heptanol	543-49-7
					2,3-Quinoxalinedione, 1,4-dihydro-6,7-dimethyl-	2474-50-2

Appendix 12. Frequently founded chemicals among 129 identified chemicals by HS/SPME-GC/MS

Compound	CAS No.	No. of products	Korea MOEL[1)] TWA (STEL), ppm, CMR	IARC[2)]	ACGIH[3)]	NTP[4)]	EU CLP[5)]
Toluene	108-88-3	29 (56.9%)	- 50 (150), Rep. 2	- Group 3	- A4		
p-Cresol	106-44-5	23 (45.1%)	- 5		- A4		
Propylene glycol monomethyl ether	107-98-2	22 (43.1%)	- 50 (150)		- A4		
Acetone	67-64-1	18 (35.3%)	- 500 (750)		- A4		
Acetic acid	64-19-7	15 (29.4%)	- 10 (15)				
Benzyl methacrylate	2495-37-6	14 (27.5%)					
Methyl isobutyl ketone	108-10-1	13 (25.5%)	- 50 (75), Car. 2	- Group 2B	- A3		
1,4-Dioxane	123-91-1	13 (25.5%)	- 20, Car. 2	- Group 2B	- A3	- R	- Car. 2
Ethyl 3-ethoxypropionate	763-69-9	12 (23.5%)					
1,2,4-Trimethylbenzene	95-63-6	12 (23.5%)					

1) Ministry Of Employment and Labor, Carcinogen classifications – Carcinogen 1A : Have sufficient evidence of carcinogen to human, Carcinogen 1B : Have sufficient evidence of carcinogen to animal or limited evidence of carcinogen to human and animal, Carcinogen 2 : Have insufficient evidence of carcinogen to human and animal
2) International Agency for Research on Cancer, Carcinogen classifications – Group 1 : Carcinogenic to humans, Group 2A : Probably carcinogenic to humans, Group 2B : Possibly carcinogenic to humans, Group 3 : Not classifiable as to its carcinogenicity to humans, Group 4 : Probably not carcinogenic to humans.
3) American Conference of Governmental Industrial Hygienists, Carcinogen classifications – A1 : Confirmed human carcinogen, A2 : Suspected human carcinogen, A3 : Confirmed animal carcinogen with unknown relevance to humans, A4 : Not classifiable as a human carcinogen, A5 : Not suspected as a human carcinogen.
4) National Toxicology Program, Carcinogen classifications – K : Know to be human carcinogens, R : Reasonable anticipated to be human carcinogens.
5) Classification, Labelling, Packing of substances and mixture, Carcinogen classifications – Carcinogen 1A : Known to have carcinogenic potential humans, Carcinogen 1B : May causes cancer, Carcinogen 2 : Suspected of causing cancer

Appendix 13. HS/SPME-GC/MS chromatogram for formaldehyde by changing temperature